CHAPTER 7

Carbon dynamics in the eutrophied Belgian Coastal Zone

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7.1 Carbon cycle in coastal waters

Net autotrophic ecosystems, where gross primary production (GPP) exceeds community respiration (CR), decrease carbon dioxide (CO_2) in the surrounding waters, while net heterotrophic systems, where GPP<CR, enrich the water in CO_2. Net ecosystem production (NEP = GPP-CR) is then one of the main drivers of the exchange of CO_2 between aquatic systems and the atmosphere. Nevertheless, in coastal environments, the link between the exchange of CO_2 with the atmosphere and the ecosystem metabolic status is not always direct (Gattuso *et al.*, 1998; Borges, 2005; Borges *et al.*, 2006). Besides NEP, the net CO_2 flux between the water column and the atmosphere is modulated by other factors such as other biogeochemical processes (*e.g.* $CaCO_3$ precipitation/dissolution), temperature and hydrodynamics (horizontal advection, down and up‑welling of waters with different CO_2 concentration, residence time, decoupling between organic carbon production and degradation within the water column).

Eutrophication manifests as a general increase of phytoplankton production and sometimes changes in planktonic composition in coastal zones (Billen *et al.*, 1991; Cloern, 2001). The effect of eutrophication on NEP and air-water CO_2 fluxes has been investigated with the one-box global Shallow-water Ocean Carbonate Model (SOCM; Andersson & Mackenzie, 2004). This model simulates a decrease of the CO_2 emission from the coastal ocean to the atmosphere since pre-industrial times and a neutral flux at present time (Andersson & Mackenzie, 2004; Mackenzie *et al.*, 2004; 2005). This evolution is explained by the combination of atmospheric CO_2 rising and NEP enhancement by the increased discharge of anthropogenic nutrients. Poorly investigated at the regional and local scale, the carbon dynamics in eutrophied coastal ecosystems is discussed in this chapter based on a synthesis of carbon

measurements and model simulations obtained in the Scheldt river plume, the Belgian Coastal Zone (BCZ) and adjacent marine waters.

7.2 Present-day carbon cycle in the Scheldt river plume

Figure 7.1 shows the time series of the partial pressure of CO_2 (pCO_2), air-water CO_2 fluxes (FCO_2) and NEP obtained in front of the Zeebrugge harbour between 2001 and 2004. As suggested by Borges and Frankignoulle (1999; 2002), this station is influenced by Scheldt waters and the observed carbon dynamics is representative of the Scheldt river plume. As shown on Figure 7.1a, surface waters are under-saturated in CO_2 with respect to atmospheric equilibrium during spring and over-saturated during the rest of the year with the maximum over-saturation observed in late-summer. The NEP seasonal evolution shows a transient but pronounced autotrophic period occurring every spring but with a different timing (early April in 2001 and 2002, mid April in 2003 and 2004) and amplitude (maximal values ranging from 134 mmol m^{-2} d^{-1} in 2004 to 269 mmol m^2 d^{-1} in 2003; Fig. 7.1c). This autotrophic period can be ascribed to the diatom-*Phaeocystis* spring bloom (*e.g.* Rousseau *et al.*, 2002; 2008). It is followed by a marked heterotrophic period corresponding to zooplankton grazing (Daro *et al.*, 2008) and bacterial degradation of the organic matter produced during spring (Rousseau *et al.*, 2002). In summer, a net autotrophic event was recorded in 2001 and 2003, and a balanced metabolic status in 2002 and 2004 (Fig. 7.1c). This variability might be explained by the year-to-year fluctuation in time and amplitude of summer phytoplankton growth (Breton *et al.* 2006; Rousseau *et al.*, 2008). Late summer is clearly characterized by net heterotrophy that decreases during fall, and a nearly balanced metabolic status is observed in winter.

At the annual scale the nearshore waters behave as a net heterotrophic system in 2001, 2002 and 2004, but autotrophic in 2003 (Table 7.1). Net heterotrophy of the Scheldt estuarine plume has been previously shown by Borges and Frankignoulle (2002) based on a simple organic carbon input/output budget. This latter suggests that CO_2 emission to the atmosphere observed in the nearshore waters is only partly due to the input of CO_2 from the Scheldt. Therefore the net heterotrophy estimated for the nearshore waters must be subsidized by external inputs of organic carbon that can originate from either coastal tributaries and/or from the Scheldt.

The potential degradation of the organic matter discharged into the BCZ by the Scheldt, estimated to 0.8-2 (Wollast, 1976) and 0.7-1.8 mol C m^{-2} yr^{-1} (Wollast, 1983), would correspond to a carbon flux of the same order of magnitude than the NEP values computed here (Table 7.1). These figures are however higher than those provided by Borges and Frankignoulle (2002) and based on the Soetaert and Herman (1995)'s estimations of organic matter discharged by the Scheldt, *i.e.* between 0.3 and 0.6 mol C m^{-2} yr^{-1} depending on the surface area of the Scheldt plume.
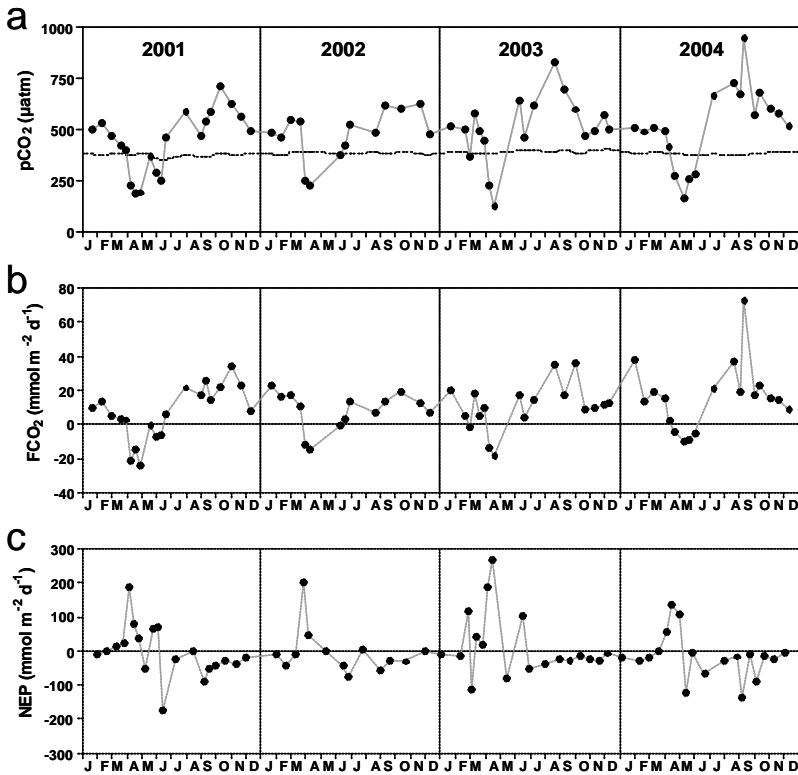
Figure 7.1 Time series of pCO_2 (a), FCO_2 (b) and NEP (c) in the Scheldt plume at a fixed station off the Zeebrugge harbour. NEP is estimated from a mass balance of dissolved inorganic carbon (Borges *et al.*, 2008).

Table 7.1. Scheldt winter freshwater discharge (Q) computed as the average of January and December of the previous year, and annual averages of pCO_2, air-sea gradient of pCO_2 ($?pCO_2$), FCO_2 and NEP at a fixed station off the Zeebrugge harbour.

	Q $m^3\ s^{-1}$	pCO_2 µatm	$?pCO_2$ µatm	FCO_2 $mol\ m^{-2}\ yr^{-1}$	NEP $mol\ m^{-2}\ yr^{-1}$
2001	348	481	107	3.6	-4.2
2002	302	480	97	3.2	-3.8
2003	393	527	136	4.6	2.4
2004	210	533	153	6.6	-5.7

The pronounced spring (Fig.7.1c) and annual (Table 7.1) NEP computed in 2003 could be due to the stronger Scheldt discharge in winter (393 m^3 s^{-1}; Table 7.1) The latter increases the delivery of nutrients from diffuse source but not of organic matter from point source stimulating therefore the GPP without modifying heterotrophy sustained by allochthonous organic carbon. Supporting this, Gypens *et al.* (2004) showed in a model study comparing two contrasted years that annual GPP in the BCZ could increase by about 27% for an increase of wintertime fresh water discharge from about 100 to 350 m^3 s^{-1}. Interestingly, despite their net autotrophic status in 2003, the nearshore coastal waters were estimated to act as net source of CO_2 for the atmosphere (Table 7.1). This confirms that a fraction of this CO_2 emission is sustained by CO_2 inputs from the Scheldt (Borges & Frankignoulle, 2002; Schiettecatte *et al.*, 2006) that would also be expected to increase with freshwater discharge.

The stronger annual heterotrophy computed for 2004 than for 2001 and 2002 could be due to a transient accumulation of part of the excess organic matter produced in 2003. Hence, we hypothesize that part of the non-steady accumulation of organic matter from 2003 to 2004 occurred in the sediments. Sedimentation of organic matter is important in the BCZ in agreement with the fact that nearshore sediments in the BCZ are exceptionally rich in organic carbon compared to the rest of the North Sea (Wollast 1976; de Haas *et al.* 2002; Vanaverbeke *et al.*, 2008).

7.3 Present-day annual budget of NEP and FCO$_2$ along the Scheldt river-Southern Bight of the North Sea continuum

Based on the present results obtained in nearshore waters influenced by the Scheldt, those of Gazeau *et al.* (2005) for the Scheldt estuary, and those of Schiettecatte *et al.* (2007) for the Southern Bight of the North Sea (SBNS), we established an annual budget of NEP and FCO$_2$ along a continuum from the Scheldt estuary to the SBNS (Fig. 7.2).

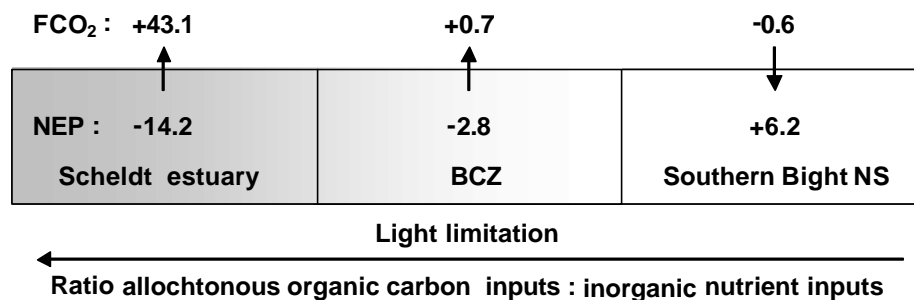Figure 7.2. Annual budgets of NEP and FCO$_2$ along a continuum from the Scheldt estuary to the SBNS (fluxes in mol m^{-2} d^{-1}), adapted from Schiettecatte (2006).

The figures obtained are in agreement with the conceptual model of Borges *et al.* (2006) whereby estuaries are strong sources of CO_2 sustained by a net heterotrophic metabolism, while temperate continental shelves act as sinks of CO_2 sustained by efficient carbon export. Also, estuaries are effective reactors for organic matter mineralisation, hence strong sources of CO_2 and inorganic nutrients to the adjacent coastal ocean that acts as a sink for atmospheric CO_2 (at temperate latitudes). Finally, this also confirms the role of physical settings in determining the auto or heterotrophic status and direction of air-sea CO_2 fluxes in river plumes, whereby well mixed systems do not export efficiently organic matter and act as sources of CO_2, while stratified river plumes export organic matter across the pycnocline and act as sinks of CO_2 (Borges, 2005).

7.4 Past evolution of carbon dynamics in the BCZ in relation to eutrophication and increased atmospheric CO_2

7.4.1 Effect of eutrophication on NEP and air-sea CO_2 fluxes

The impact of changing human activities on the watershed and increased atmospheric CO_2 over the past 50 years on the role as sink or source for atmospheric CO_2 of the BCZ was investigated using a coupled river-coastal model. The R-MIRO-CO_2 model results from the off-line coupling between two biogeochemical models, the RIVERSTRAHLER river model (*e.g.* Billen *et al.*, 1994) and the marine MIRO model (Lancelot *et al.*, 2005) including a description of the carbonate system (MIRO-CO_2; Gypens *et al.*, 2004). Details on the coupling between RIVERSTRAHLER and MIRO are provided in Lancelot *et al.* (2007). For this application, the R-MIRO-CO_2 model was implemented in a multi-box frame from the Eastern Channel to the Belgian coastal zone (Fig. 6.2). Model simulations were performed using daily wind speed and sea surface temperature and monthly atmospheric CO_2. Nutrient river inputs were provided by the RIVERSTRAHLER model applied to the Seine and Scheldt river systems. RIVERSTRAHLER implementation and description of meteorological forcing and nutrient point and diffuse sources at the scale of the Seine and Scheldt river systems over the past 50 years are reported in respectively Billen *et al.* (2001) and Billen *et al.* (2005). For both basins, the following forcing functions to the model were documented for the period 1950-2000: year-to-year variation of rainfall by 10 days period; land use modifications by 10 year period; changes in annual urban and industrial wastewater discharges by 5 year period. Model results are here shown in terms of historical evolution of nutrient and carbon loads as well as annual air-sea CO_2 fluxes and NEP simulated in the BCZ.
Figure 7.3 shows the evolution of total nitrogen (Ntot), phosphorus (Ptot), dissolved silicate (DSi) and organic carbon annual loads simulated by the RIVERSTRAHLER model for the Seine and the Scheldt rivers between 1951 and 1998. The annual carbon and nutrient fluxes delivered by both rivers show similar trend but the magnitude of the nutrient loads delivered by the Seine is higher than by the Scheldt (about 5, 10 and 3 times respectively, for Ntot, Ptot and DSi). This results from the higher water discharge of the Seine while

nutrient concentrations are similar in both rivers (not shown). However, the organic carbon inputs from the Scheldt are up to three times higher than the Seine loads during the eighties (Fig. 7.3.d).
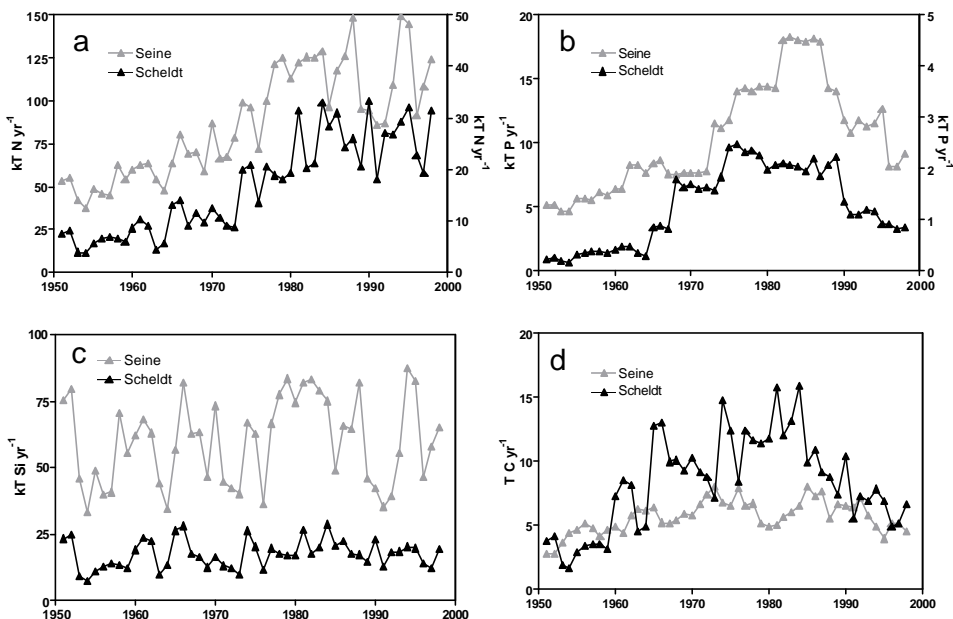

Figure 7.3. Evolution between 1951 and 1998 of Ntot (a), Ptot (b), DSi (c) and organic carbon (d) annual loads from the Seine and the Scheldt. Seine: left scale; Scheldt: right scale.

Although some part of the nutrient and organic carbon loads inter-annual variability can be attributed to the river discharge (not shown), the long-term trend simulated over the past 48 years results from the changing nutrient and carbon emissions to surface water in response to modification of human activities on the watershed. From 1950 to 1965, Ntot, Ptot and DSi loads stay relatively constant both for the Seine and the Scheldt rivers (Fig. 7.3). As a result of the combined effect of increasing leaching of agricultural soils and rising emissions from domestic and industrial activities (Billen *et al.*, 2001; 2005), the annual Ntot fluxes delivered by the Seine show, after 1965, a clear increase up to values greater than 100 kt N yr^{-1} during the 1990's (Fig. 7.3.a). A similar increase is simulated for the Scheldt with annual Ntot loads reaching 30 kt N yr^{-1} in 1990. In parallel, annual Ptot loads from the Seine and the Scheldt increase by a factor 5 between 1965 and 1985 (Fig. 7.3.b). After 1985, P loads progressively decrease until 1998 when values corresponding to those simulated in 1960's are obtained. This decrease results from the removal of PO_4 in washing powders as well as the improved treatment of urban effluents (Billen *et al.*, 2001; 2005). The simulated inter-annual variability of dissolved silicate (DSi) loads (Fig. 7.3.c) is mainly driven by river discharges (not shown) while

the river DSi concentration stays relatively constant. Organic carbon loads, as Ntot and Ptot loads, show, after 1960, a marked increase in response to human development in the watershed before decreasing in the mid-eighties due to the implementation of waste water treatment plants (Fig. 7.3.d).

R-MIRO-CO_2 simulations obtained for the BCZ (Fig. 7.4) show marked historical changes in both NEP and air-sea CO_2 fluxes. Annual NEP shows important inter-annual fluctuations, with annual simulated values ranging between -1.24 and + 0.44 mol C m^{-2} yr^{-1} in respectively 1966 and 1992 (Fig. 7.4). From 1950 to 1967, the BCZ is shown as net heterotrophic with NEP values between -0.68 and -1.24 mol C m^{-2} yr^{-1}. From 1967 to 1982, the BCZ ecosystem is still heterotrophic but the NEP strongly decreases to value near zero (-0.2 mol C m^{-2} yr^{-1}). Over the next ten years (1983-1993), the BCZ is shifted from net heterotrophy to net autotrophy and NEP values of +0.3 mol C m^{-2} yr^{-1} are simulated in 1989 and 1992. After 1993, the system returns to heterotrophy up to the end of the simulated period and NEP values are close to those simulated before 1967 except in 1996 (Fig. 7.4).

The simulated annual air-sea CO_2 fluxes also show important inter-annual fluctuations between 1951 and 1998 (Fig. 7.4). Air-sea CO_2 flux simulated by the model is positive when the flux is directed from the sea to the atmosphere meaning that the BCZ acts as a source for atmospheric CO_2. From 1951 to 1970, the BCZ is clearly releasing CO_2 towards the atmosphere when estimated on an annual basis. The magnitude of this source ranges between 0.03 and 0.5 mol C m^2 yr^{-1} without any clear trend. The simulated trend of annual air-sea CO_2 flux decrease to values close to zero between 1970 and 1974 after which it reverses to negative values (Fig. 7.4). From 1975 to 1993, the BCZ is a net sink for atmospheric CO_2 with a maximal value of -0.4 mol C m^{-2} yr^{-1} in 1985. After 1985, the magnitude of the sink gradually decreases and, between 1994 and 1998, the BCZ becomes again a net source of CO_2 excepted in 1996.
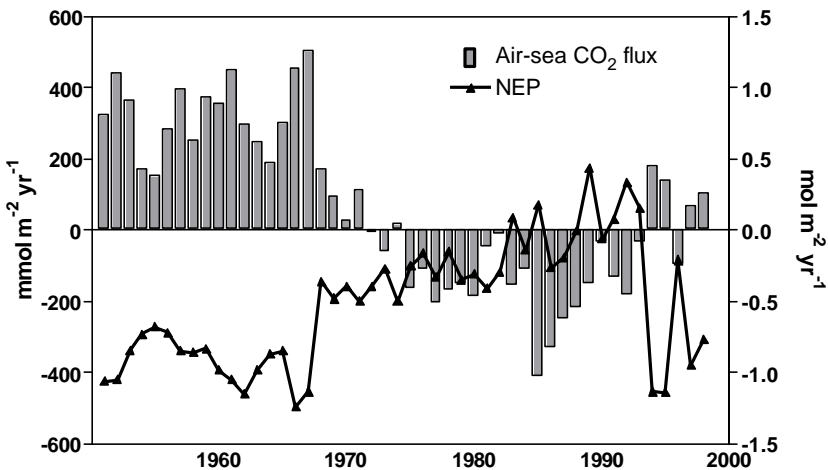

Figure 7.4. Evolution between 1951 and 1998 of annual air-sea CO_2 fluxes (left scale) and NEP (right scale) in the BCZ.

7.4.2 Factors affecting air-sea CO_2 fluxes variability in the eutrophied BCZ

Seawater temperature, wind speed, atmospheric CO_2 and carbon and nutrient loads directly or/and indirectly are constraining air-sea CO_2 fluxes. While wind speed and atmospheric CO_2 only directly affect carbonate chemistry, carbon, nutrients and temperature also indirectly modulate the magnitude of this flux by controlling autotrophic and heterotrophic activities in the water column. The importance of the variability of these forcings for the simulated air-sea CO_2 flux in the BCZ is estimated by comparison to their importance in 1951. The contribution of each forcing to the annual air-sea CO_2 flux variability is investigated based on the comparison between model results obtained using real forcing for the 1951-1998 period and those obtained by running R-MIRO-CO_2 with the 1951 values of either temperature, wind speed, atmospheric CO_2 or carbon and/or nutrient loads for each year of the considered period.

The comparison of annual air-sea CO_2 fluxes simulated using real and 1951 values of temperature, wind speed and atmospheric pCO_2 suggests that the inter-annual variability of these forcings has no significant influence on the magnitude and the direction of the simulated air-sea CO_2 flux for the 1951-1998 period (not shown). Similarly, temperature variability has no major influence on long-term trend of NEP (not shown).

Most of the variability of air-sea CO_2 fluxes computed with the R-MIRO-CO_2 model between 1951 and 1998 is due to river loads (Fig. 7.5). When compared to the reference simulation, the use of 1951 nutrient and carbon loads for both the Seine and the Scheldt leads to an important modification of the magnitude and the direction of the annual air-sea CO_2 flux. When using 1951 river loads (carbon and nutrients) for each year of the simulated period, BCZ is annually net heterotrophic (not shown) and acts as a source for CO_2 during the whole period. Comparison of annual air-sea CO_2 fluxes obtained when using real and 1951 river loads shows that river loads increase the autotrophy and the sink capacity of the BCZ from 1951 to 1998. The magnitude of this sink stays relatively constant between 1951 and 1967, after what it progressively increases up to 1992 when river loads are maximal. Increase of the sink due to river loads can be related to both N and P load increases. After 1992, the decrease of P loads, in spite of sustained elevated N ones, limits primary production (Lancelot *et al.*, 2007) in the BCZ and the associated air-sea CO_2 sink. This imbalance in N and P delivery explains the simulated CO_2 source from 1993 to 1998.

As a general pattern, the simulated magnitude of air-sea CO_2 fluxes in the BCZ is significantly related to the variations of the nutrient and carbon loads from the Seine and the Scheldt. When comparing the respective effect of Seine and Scheldt loads variability on the air-sea CO_2 flux, the model results evidence a similar impact of both rivers during the 1950's after which the Seine is suggested to have a larger influence on the simulated annual air-sea CO_2 flux in the BCZ.
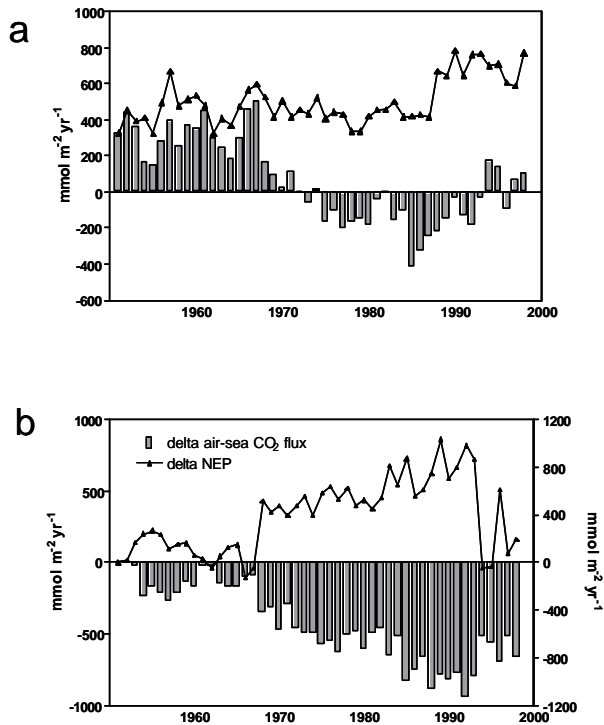
Figure 7.5. Relative contribution of carbon and nutrient river loads to air-sea CO_2 fluxes computed from 1951 to 1998. Comparison of air-sea CO_2 fluxes computed using real forcing (grey bar) and 1951 (triangle) value for Seine and Scheldt river loads (a) and the delta air-sea CO_2 flux (grey bar) and delta annual NEP (triangle) computed as the difference between model results obtained using real and 1951 carbon and nutrient loads (b).

7.5 Conclusions

Using an observation-based approach and a modeling tool, we show that air-water CO_2 fluxes and NEP are subject to strong inter-annual variability in the BCZ mainly driven by riverine inputs of nutrients. We also show that NEP is one of the main drivers of air-water CO_2 fluxes in the BCZ but there is not a perfect match between direction of the CO_2 fluxes and the ecosystem autotrophic or heterotrophic status. Nevertheless, both approaches are converging and suggest that, for present day conditions, the BCZ is net heterotrophic and acts as a source of CO_2 to the atmosphere.

The reconstruction of NEP and air-water CO_2 fluxes over the last 50 years suggests that the BCZ shifted from a CO_2 source during the 1960's and 1970's to a sink during the 1980's and 1990's, explained by increased eutrophication. Due to imbalanced nitrogen to phosphorus loads, the BCZ shifted back to a CO_2 source in the late 1990's. While eutrophication during the 1970's and 1980's leads to quantitative and qualitative phytoplankton changes with undesirable

effects (Lancelot, 1995; Lancelot *et al.*, 2007), our model results suggest that it was accompanied by a strong carbon sink.

This points an important but so far neglected coupling between nutrient regulation and mitigation of the emission of greenhouse gases that must be evaluated jointly in management policies. We also show that the link between nutrient delivery to the coastal zone and atmospheric carbon pumping is complex. Sustained long-term monitoring along inshore-offshore gradients is then required to further unravel and constrain this link and to refine and validate model tools to improve predictions on the future evolution of biogeochemical functioning of the coastal zone and hence guide decision makers and managers.

7.6 References

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